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Interfaces in Polyethylene Oxide Modified Cellulose Nanocrystal - Polyethylene Matrix Composites

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Abstract The interface between cellulose nanocrystals (CNCs) in thermoplastic matrices is one of the most important issues in the development of CNC-based polymeric composites prepared via melt processing. In the present work, polyethylene oxide (PEO) was used as a compatibilizer to enhance the interface with a polyethylene matrix. It was found that the composites produced using a PEO compatibilizer possess better overall mechanical properties and a higher degree of crystallinity of polyethylene than the unmodified samples. An increase in both the tensile strength and modulus of the composites was observed for up to 1.5 wt.% of CNCs; beyond this point no significant increases were observed. When CNCs are added (up to 1.5 wt. %) to the matrix, the crystallization peak of the composites in the DSC thermograms is shifted to higher temperatures. The stress-transfer process in the composites was monitored using Raman spectroscopy. Higher Raman band shift rates with respect to tensile strain of a peak corresponding to main chain molecular deformation are observed for the composites produced using the PEO compatibilizer. This demonstrates that stress is transferred from the matrix to the fillers more effectively with the presence of PEO. The simple PEO-modification approach adopted in this study avoids the classical solvent method of

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production of CNC-based nanocomposites which is not really applicable at an industrial scale.

Keywords: Cellulose nanocrystals (CNCs); Polyethylene oxide; Melt compounding; Dispersion

1. Introduction

Biobased nanofillers for the development of polymer-based nanocomposites have attracted a large amount of research interest in recent years because of their great potential for producing a variety of high-value products with low impact on the environment. The potentially superior mechanical properties of cellulose nanocrystals (CNCs) compared to micron-sized fibres, make them ideal candidates as reinforcing fillers for polymeric matrices [1]. Wet processing methods such as casting/evaporation are widely applied in most studies for the fabrication of the CNCs reinforced composites [2, 3]. The main advantage of these approaches is the preservation of the dispersed state of nanoparticles in the liquid medium and later in the polymeric matrix. This approach to disperse nanoparticles in thermoplastic matrices is however, to the most part, both non-economic and non-scalable on an industrial level. Melt compounding techniques such as extrusion or injection moulding are the industrial approach of choice that would allow the manufacture of a large range of products because they could potentially be produced rapidly, cheaply and in a range of different shapes. It is noted that some success has been had in combining thermally stable CNCs in melt processing, even reporting comparable results with solution casting approaches [4]. There are however several major challenges to overcome before CNCs can be effectively incorporated into a thermoplastic polymer matrix during melt processing. One challenge is related to the highly hydrophilic

character of CNCs which inhibits their mixing and dispersion with hydrophobic thermoplastic matrices. If blended mechanically, these two components may result in poor mechanical properties owing to their incompatibility. The addition of compatibilizers such as maleic anhydride, polyoxyethylene, polyethylene glycol has been shown to improve the compatibility between these two phases [5-7]. In terms of the characterisation of nanocellulose-thermoplastic composite interfaces, most researchers have focused on studies of their morphology, mechanical properties, crystallinity, thereby inferring the nature of the interactions between the filler and matrix. Very limited studies have been reported on quantifying the interfacial micromechanics of thermoplastic-cellulose nanocrystal composites. Most studies have reported thermoset or solution cast matrix systems [8-10]. No work has been published to date on quantifying the stress-transfer process in a thermoplastic CNCs reinforced composite system. In this paper, we present a non-contact Raman spectroscopy method to characterise the stress-transfer in melt processed nanocomposites. These nanocomposites comprise a nonpolar polymer matrix of high density polyethylene (HDPE) and CNCs using polyethylene oxide (PEO) as compatibilizer. For the first time, it has been possible to fully characterise the interface between a thermoplastic matrix and CNCs, elucidating the effect of this interesting compatibilization system.

2. Experimental

2.1. Materials

Whatman No. 1 filter paper as a source of cotton cellulose, sulfuric acid (purity 98%) and Poly(ethylene oxide) (PEO) with a molecular weight of $5 \times 10^6 \text{ g mol}^{-1}$ were purchased

from Sigma Aldrich (Dorset, UK). High density polyethylene (Arboblend HDPE) was supplied by Tecnar GmbH (Ilsfeld, Germany).

2.2. Preparation of Cellulose Nanocrystals (CNCs)

CNCs were isolated from Whatman No. 1 filter paper following a procedure that has been described previously [11]. Briefly, 5.2 g of filter paper was blended with 250 mL of deionized water to form a pulp. Sulfuric acid (140 mL) was slowly added to this pulp under vigorous mechanical stirring (250 mL, 20 °C). The resulting suspension was held at 50 °C and magnetically stirred for 3.5 hours to allow hydrolysis to take place. After hydrolysis, the mixture was cooled at room temperature and washed via centrifugation at 3400 rpm for 15 minutes. This process was repeated until the solution had a pH 3-4. The solution was then dialyzed against distilled water **until a pH value of 7 was obtained**. Then the dispersion was sonicated for approximately 6h. The resulting suspensions were stored at 4 °C or freeze dried till further use. Freeze drying, or some form of drying, is required to remove as much moisture as possible before compounding. There are methods for solvent exchange and incorporation of CNCs into a melt-mixing protocol [11, 12]. We were however aiming to attempt to form composites from dried CNCs, for potential industrial scalability.

2.3. Preparation of Composite Materials

Aqueous polymer solutions were obtained by adding PEO into distilled water (1.25 wt.%) and magnetic stirring at room temperature. This solution was then protected from photo-oxidation by covering with aluminium foil [13]. The solution was then weakly stirred at 500 rpm for 4 days. After the aqueous PEO solutions were prepared, CNCs also in an

aqueous suspension were added (50:50 PEO:dry CNCs based on PEO amount). Then, distilled water was added to ensure the resulting suspension of PEO/CNCs had an overall PEO concentration of 1 wt.%. These suspensions were then freeze dried before compounding and extrusion. Freeze drying was necessary to eliminate water from the materials before compounding, and to also assist the adsorption of PEO onto the surface of the CNCs.

The filler, compatibilizer and matrix were mixed in a mortar for 8 minutes. This mixture was then dried in a vacuum oven at a temperature of 60 °C for 24 h to remove humidity. Nanocomposites were prepared by mixing HDPE and either unmodified or PEO-modified CNCs (nanocellulose content ranging from 0 to 5 % based on HDPE content) using a counter rotating, intermeshing twin screw extruder (Haake, MiniLab Rheomex CTW5, Thermo Fisher Scientific). The mixing speed was set at 70 rpm for 7 min and the matrix component was melt processed at 160 °C. The composites were extruded in filament form with a diameter of ~2 mm. These filaments were cut into ~2 mm lengths which were subsequently hot pressed at the same temperature with a pressure of 5 MPa for 5 min to form nanocomposite sheets with nominal thicknesses of ~0.25 mm.

2.4. Electron Microscopy of Materials

A transmission electron microscope (JOEL-200FX) was used to examine the CNCs samples at an accelerating voltage of 120 kV. An aqueous CNC solution was deposited onto a holey carbon coated grid and then negatively stained by allowing the grids to float in a 2% uranyl diacetate solution for 3 minutes. The dimension of the CNCs were determined from the TEM images by using image analysis software (ImageJ).

2.5. Thermo Gravimetric Analysis

The thermal stabilities of the unmodified-CNCs and PEO-modified CNCs were studied using thermogravimetric analysis (TGA), Mettler Toledo TGA/DSC 1, STAR^e System. Samples with masses in the range of 10 to 12 mg were heated under a nitrogen flow of 50 ml min⁻¹ from 30 to 600 °C at a heating rate of 10 °C min⁻¹, and the corresponding mass loss was recorded.

2.6. Crystallinity of Composite Materials

A Mettler Toledo (DSC721e) differential scanning calorimeter was used to investigate the thermal properties of neat HDPE and CNCs reinforced composites. Samples weighing 10 - 15 mg were enclosed in hermetically sealed aluminium pans. They were heated under a nitrogen flow of 50 ml min⁻¹ from 25 to 200 °C at a heating rate of 10 °C min⁻¹, kept at this temperature for 5 min to erase the thermal history, cooled to 25 °C at the same rate, and reheated under the same conditions. The melting enthalpies (ΔH_m) and temperatures (T_m) were determined from the second heating curve, while the crystallization enthalpies (ΔH_c) and temperatures (T_c) of the samples were determined from the first cooling curve. Three individual measurements were performed to ensure reproducibility. The degree of crystallinity of the HDPE was calculated using the equation

$$\chi_c(\%) = \frac{\Delta H_m}{(1-\phi)\Delta H_m^0} \times 100 \quad (1)$$

where ΔH_m is the enthalpy of melting, ΔH_m^0 is the enthalpy corresponding to the melting of 100% crystalline HDPE (=293.6 J/g) [14] and ϕ is the weight fraction of filler.

2.7. Mechanical Properties of Composites

Mechanical deformation of the composite samples was carried out using a Lloyd Universal Testing Machine according to a standard method (ASTM D 882-02) in order to determine their tensile properties. A specimen size $50 \times 5 \times 0.25$ mm was used for these tests. Seven samples were tested for each weight fraction and for each form of nanocomposite. A testing speed of 10 mm/min and a load cell of 500 N was used in all cases.

2.8. Composite Micromechanics Using Raman Spectroscopy

For micromechanical testing, a Renishaw 1000 Raman spectrometer equipped with a thermoelectrically cooled CCD detector was utilized to record spectra. Thin films of the nanocomposites ($20 \times 2 \times 0.25$ mm) were incrementally deformed using a Deben rig (Deben UK Ltd) with an attached 200 N load cell. Strain (defined as the change in length of specimen divided by the original length) was incremented by 0.5% before each Raman spectrum was recorded. Raman spectra were recorded *in situ* after each deformation step. A near-IR laser with a wavelength of 785 nm was used to record spectra from the nanocomposites using an exposure time of 30 s and four accumulations. The laser beam was focused using a 50 \times long working distance objective lens to a spot size of $\sim 1\text{--}2$ μm . Raman spectra were acquired in the range 950 to 1550 cm^{-1} , which includes a band located at ~ 1095 cm^{-1} , which is assigned to a cellulose ring-stretching mode [15]; 3 spectra were recorded at each strain increment. A Lorentzian function was used to fit this Raman band to find its position as a function of strain. The incident and scattered laser light were polarised parallel to the principal axis of the spectrometer and to the long axis of the samples and, therefore, also to the tensile deformation axis of the specimens.

3. Results and discussion

3.1 Morphology of cellulose nanocrystals

A TEM micrograph of a deposited aqueous suspension of CNCs is presented in Figure 1a. Fifty measurements of the widths and lengths of the CNCs were recorded and averaged; these were found to be 14.3 ± 3.6 nm and 165.5 ± 38.3 nm respectively.

3.2 Physical Properties of unmodified and PEO-modified CNCs

Unmodified-CNCs formed a white powder after freeze drying (Figure 1b) and PEO-modified CNCs formed a dense and ‘spongy’ material (Figure 1c). It was also observed that PEO-modified CNCs deformed semi-elastically upon applying a force, showing some shape-memory characteristics.

3.3 Thermal stability

One of the important issues for the melt processing of sulfuric acid hydrolysed CNCs reinforced polymer nanocomposites is their thermal stability. TGA experiments were performed to investigate this property. For neat CNCs, an initial weight loss is observed upon heating from 60 °C to 190 °C (Figure 2). It is attributed to the removal of moisture in the material, due to the hydrophilic character of cellulose. At higher temperatures, a gradual weight loss in the range 200 – 350 °C was reported. It has been reported that the presence of sulphate half ester groups resulting from the sulfuric acid hydrolysis process lower the thermal stability of CNCs [16].

Pure PEO displayed a much higher thermal stability than CNCs, with a sharp weight loss within a narrow temperature range around 350 °C. The char residue (around 8%) is much lower compared to unmodified CNCs. The PEO-modified CNC mixture showed

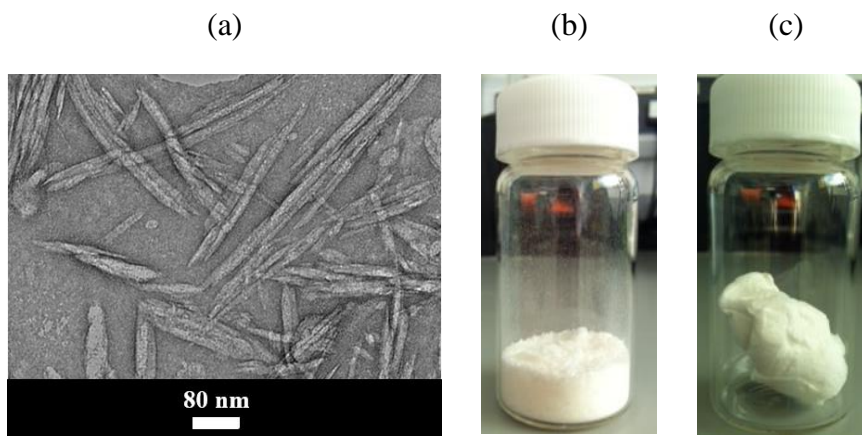


Figure 1 (a) A typical TEM image of the CNCs; Typical appearance of freeze dried CNCs samples consisting of (b) unmodified-CNCs and (c) PEO-modified CNCs.

intermediate behaviour, with an improved thermal stability compared to unmodified CNCs. This improvement is exhibited by an increase in the temperature at which the weight loss transitions occur (Fig. 2). The thermal decomposition temperatures, associated to the weight loss are shown in Table 1S (Supplementary Information). This increased thermal stability is probably due to the protecting role of interacting PEO chains that shield the sulphate half ester groups on the CNCs. PEO is a polar polymeric chain, with known hydrogen bond interactions occurring between the primary hydroxyls at the C6 position in model cellulose compounds (not cellulose itself though) and the ether oxygen in the PEO chain [17]. It is thought that a shielding of the sulphate half ester groups takes place, although a separate interaction with this group and the ether oxygen in PEO may also occur.

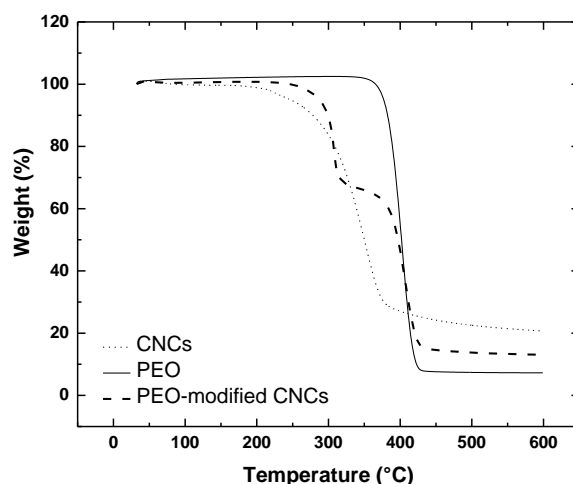


Figure 2 Thermal Gravimetric Analysis (TGA) curves of CNCs, PEO and PEO-modified CNCs.

3.4. Crystallinity of Nanocomposite Materials

Crystallinity of the matrix, as affected by the incorporation of the filler material, is an important characteristic influencing the mechanical properties of nanocomposites. The crystallisation behavior of HDPE in the nanocomposites was investigated using DSC analysis. The percent crystallinity of HDPE and the nanocomposites (Table 2S, Supplementary Information and Figure 3) showed that melt compounded material (with values of ~62%) have comparable values to those reported in the literature [18, 19]. The addition of CNCs to the matrix material increases the crystallinity of the samples at low filler loadings. It is thought that the nucleation effect of CNCs leads to an increase of crystallinity of composites at low filler loadings. However, at high CNCs concentrations, the crystallinity starts to decrease, possibly due to their aggregation. Statistical significances (P-values) based on *t*-tests have been calculated to compare the crystallinity values of unmodified and modified CNCs composites. If an acceptable level of

significance is $p < 0.05$ (>95% confidence), most of the compared results are statistically significant. When using the compatibilizer, a significant increase in crystallinity was observed compared to unmodified-CNCs/HDPE, possibly due to the enhanced chain mobility of the HDPE polymer [19]. This behavior is in agreement with previous work for thermoplastic film reinforced with unmodified-CNC and PEO-modified CNC composites [7]. The nucleation effect of CNCs is also demonstrated by the cooling thermograms in Figure 4. The maxima of the crystallization peaks of the composites are shifted to higher temperatures when CNCs are added until 1.5 wt%. Above this filler loading, the peak temperature shows no further significant increase.

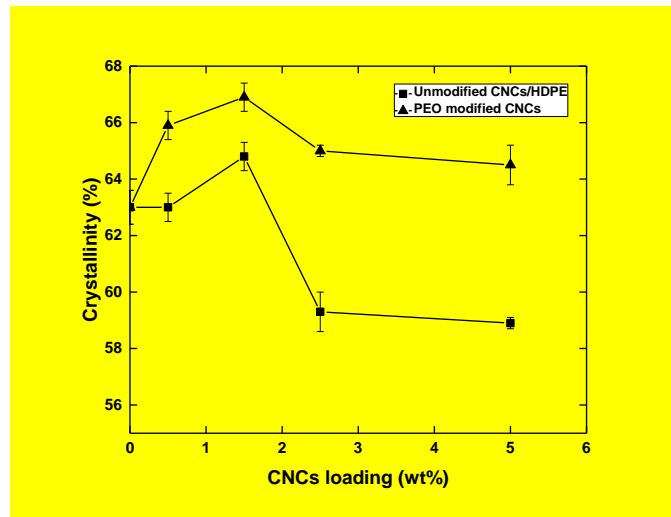


Figure 3 Crystallinity of unmodified-CNCs/HDPE and PEO modified CNCs nanocomposite films investigated using DSC.

3.5. Mechanical Properties of Composites

The variation of tensile modulus, strength and elongation at break for unmodified-CNC and PEO-modified CNC/HDPE composites is reported in Figure 5. The tensile modulus

and strength of the nanocomposites increased with an increasing CNCs content up to a 1.5 wt% loading for all specimens. Some of this improvement in tensile modulus

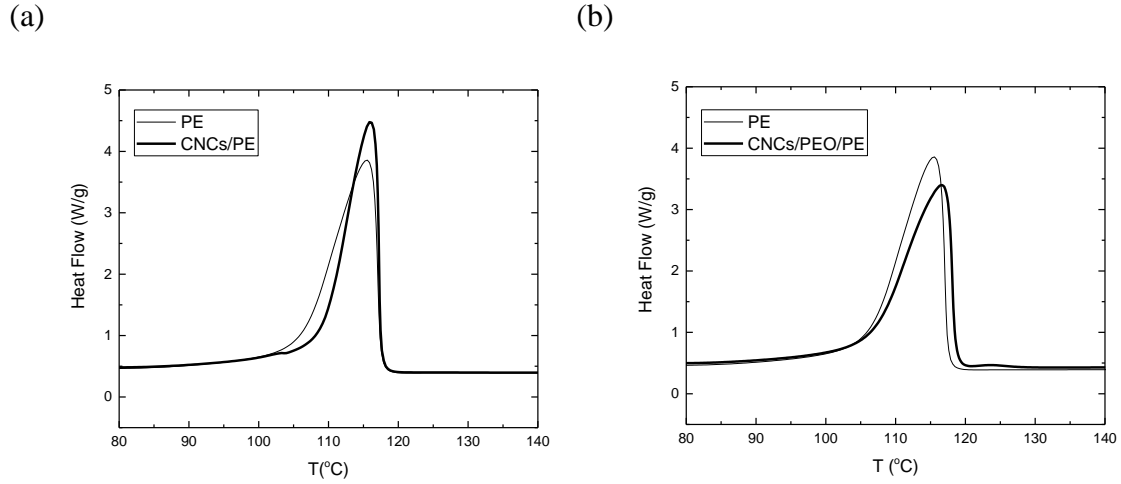


Figure 4 Typical Differential Scanning Calorimetry (DSC) thermograms for the non-isothermal crystallisation of (a) unmodified-CNCs (CNCs/PE), and (b) PEO-modified CNC/HDPE (CNCs/PEO/PE). Data are for 0% (PE) and 5% CNCs only for clarity.

and strength is possibly due to the high elastic modulus (57 - 105 GPa), and presumably strength of the crystalline CNCs [20], although the increase in crystallinity of the matrix is also noted. However, above 1.5 wt% CNCs, Young's modulus and tensile strength continuously decrease with an increasing CNCs content. This indicates that a 1.5 wt % of CNCs loading is an optimum level of addition of filler into the HDPE matrix.

Based on t-tests ($p < 0.05$), the mean values of the PEO-modified CNC/HDPE composites exhibited a significantly higher modulus and strength than the unmodified-CNCs. Therefore, it can be concluded that the addition of compatibilizer significantly enhances the tensile properties of the materials, which could be attributed to better interfacial adhesion, enhanced chain mobility and increases in the crystallinity of the matrix. Similar

observations were made when a poly(ethylene oxide)-b-poly- (propylene oxide)-b-poly(ethylene oxide) triblock copolymer was used to modify the surface of CNC; the rubbery modulus (25 °C) of composites made with a low density polyethylene (LDPE) matrix significantly increased as a result of improved dispersion of the CNC and favourable interaction with the matrix [21]. Volk *et al.* [22] reported an improvement in tensile and storage modulus of linear low density polyethylene (LLDPE) with surface treated cellulose nano-fibers. They suggested that the presence of the poly(ethylene glycol)-b-polyethylene (PEG-b-PE) polymer effectively hindered the aggregation of the cellulose nanofiber during its extrusion with LLDPE [22]. Pereda *et al.* showed improved dispersibility of CNC by the surface adsorption of PEO in extruded LDPE, although very little improvement in tensile modulus and strength were reported [23].

A significant decrease in strain at break was seen for all the nanocomposites, indicating increased brittleness of the composites after incorporating the CNCs filler into the matrix. For compatibilized nanocomposites, the strain at break values are still higher compared to unmodified-CNCs/HDPE.

3.6. Composite Micromechanics Using Raman Spectroscopy

Raman spectroscopy was used in this study to follow the micromechanical deformation of the composites. Typical Raman spectra in the wavenumber region between 225–1700 cm^{-1} for the CNCs, HDPE and composites with 5 wt.% of CNCs are presented in Figure 6. The Raman band initially located at $\sim 1095 \text{ cm}^{-1}$ is characteristic of cellulose, and corresponds to the C–O ring stretching modes and the glycosidic (C–O–C) bond stretching within the cellulose chains [15], and can be used to identify this material within a polymer matrix [24]. Other Raman bands indicative of the presence of cellulose are the

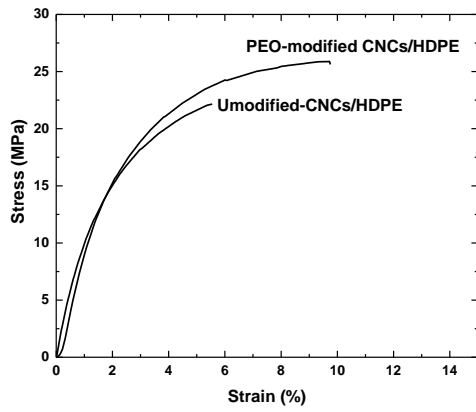
less intense peaks located in the region $250 - 600 \text{ cm}^{-1}$ assigned to skeletal-bending modes involving the C-C-C, C-O-C, O-C-C and skeletal stretching modes of C-C and C-O moieties [15]. The main band corresponding to polyethylene; is a narrow crystalline band located at $\sim 1296 \text{ cm}^{-1}$ corresponding to CH_2 twisting modes [25].

Additionally, the Raman bands located at $\sim 1063 \text{ cm}^{-1}$ and $\sim 1132 \text{ cm}^{-1}$ are assigned to C-C stretching modes representative of crystalline and amorphous phases of HDPE. Composites with different weight fractions of CNCs were deformed incrementally using 0.5% strain steps. At each incremental strain level, Raman spectra were recorded. Typical Raman spectra for PEO-modified CNCs nanocomposites before and after deformation (12% strain) are shown in Figure 7.

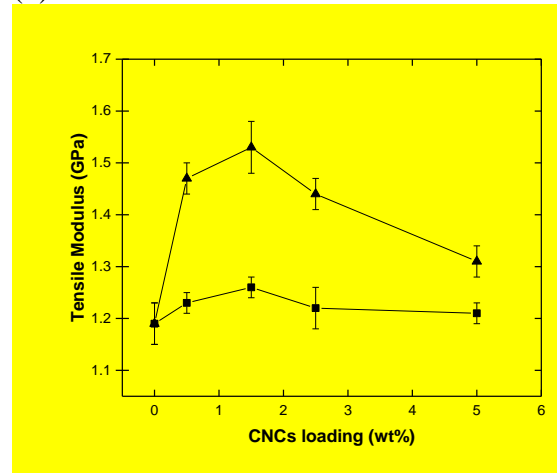
When composites were subjected to tensile deformation, the Raman band initially located at $\sim 1095 \text{ cm}^{-1}$ was observed to shift towards a lower wavenumber position. This shift indicates the stress transfers between the HDPE matrix and the CNCs in the composites, resulting in a direct deformation along the molecular backbone of the cellulose polymer [9, 20]. The profiles of these shifts are linear for the pure polymer and non-PEO modified samples. However, the data for the PEO-modified samples have a non-linear shape, and most closely reflect the shape of the stress strain curves shown in Figure 5(a). The non-linearity occurs at higher strain, and may be due to a breakdown in the interface between the softer phase of the PEO and the HDPE.

The initial gradient of the shifts in these data were determined by fitting a nonlinear quadratic equation and then taking its first differential. The magnitudes of these initial

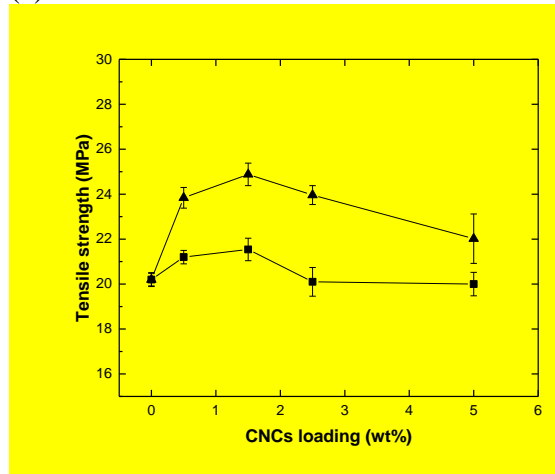
(a)



(b)



(c)



(d)

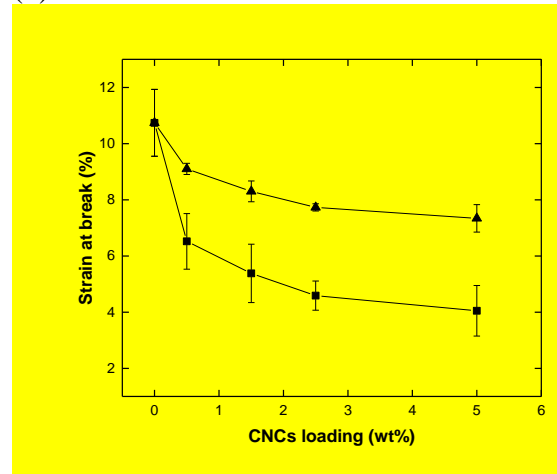


Figure 5 Tensile properties of the composite films with unmodified-CNC (■) and PEO-modified CNC/HDPE (▲) composites; (a) stress-strain curves, (b) tensile modulus, (c) tensile strength and (d) strain at break.

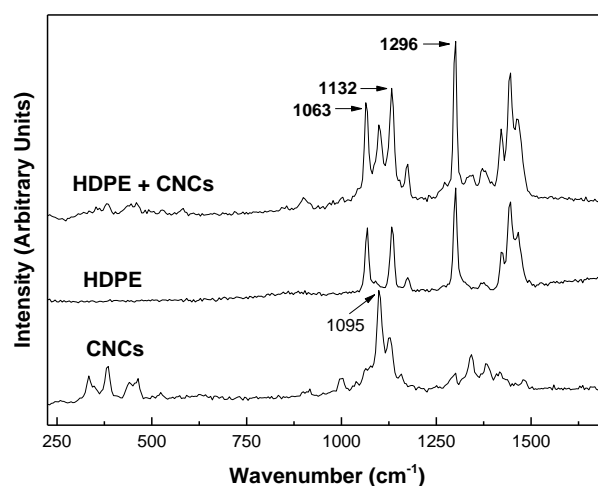


Figure 6 Typical Raman spectra of composite components; high density polyethylene (HDPE), cellulose nanocrystal reinforced HDPE (CNCs + HDPE) and cellulose nanocrystals (CNCs). Significant Raman bands (located at ~ 1095 , 1063 , 1132 and 1296 cm^{-1} are labelled for clarity).

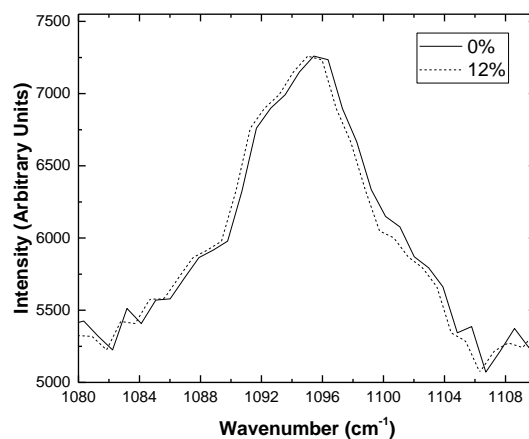


Figure 7 Typical shift in the position of the Raman band initially located at ~ 1095 cm^{-1} for a PEO-modified CNCs (1.5 wt%).

gradients are an indication of the stiffness of the composites, and thereby the level of stress transfer taking place within the material. If there is an intact interface between

the matrix and the reinforcing phase a shift in a peak representing the latter will occur to a greater or lesser extent depending on the stress transfer efficiency. However, it is true to say that a very stiff phase could be debonded from the matrix and therefore very little shift would occur. It is also true that orientation of the matrix phase, or a change in crystallinity, leading to a stiffer composite, without an increase in these initial gradients, may also occur if the interface is not intact.

A comparison between shifts in the position of the Raman band initially located at $\sim 1095 \text{ cm}^{-1}$ as a function of tensile strain for pure HDPE and nanocomposites are shown in Figure 8; data for 1.5 wt. % unmodified and PEO-modified CNCs are reported. The initial gradients of the shifts for the PEO-modified CNCs are found to be higher than for unmodified CNCs nanocomposites, an indication of the enhanced stress transfer taking place due to compatibilization. This is in agreement with the results from the tensile tests in Section 3.5; the mechanical properties of nanocomposites made from PEO-modified CNCs were higher than those produced from unmodified CNCs.

The effect of the weight fraction of CNCs on the rate of shift with respect to strain of the Raman band initially located at $\sim 1095 \text{ cm}^{-1}$, for unmodified and PEO-modified CNCs nanocomposites are shown in Figures 9a and 9b. The largest initial gradients for both unmodified-CNCs and PEO-modified CNCs nanocomposites are found to be $-0.45 \text{ cm}^{-1}\%$ and $-0.7 \text{ cm}^{-1}\%$ respectively, at a weight fraction of 1.5%. However, above 1.5 wt% of CNCs, the shift rate decreases with an increasing CNCs content (see Supplementary Information, Figure 1S). A decrease in the initial gradient with respect to strain has been found for both nanocomposites, and is thought to be due to the aggregation of CNCs at higher weight fractions.

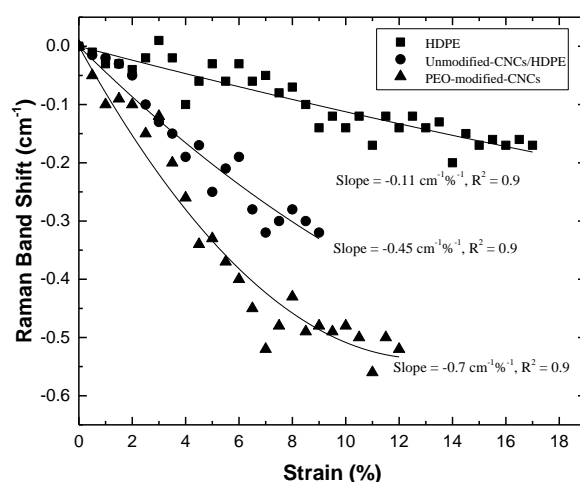


Figure 8 Typical shifts in the positions of Raman bands as a function of tensile strain initially located at $\sim 1132 \text{ cm}^{-1}$ for the pure polyethylene matrix material and at $\sim 1095 \text{ cm}^{-1}$ for unmodified and PEO-modified CNCs with 1.5 wt% CNCs. Data are fitted with a 2nd order quadratic equation (solid line).

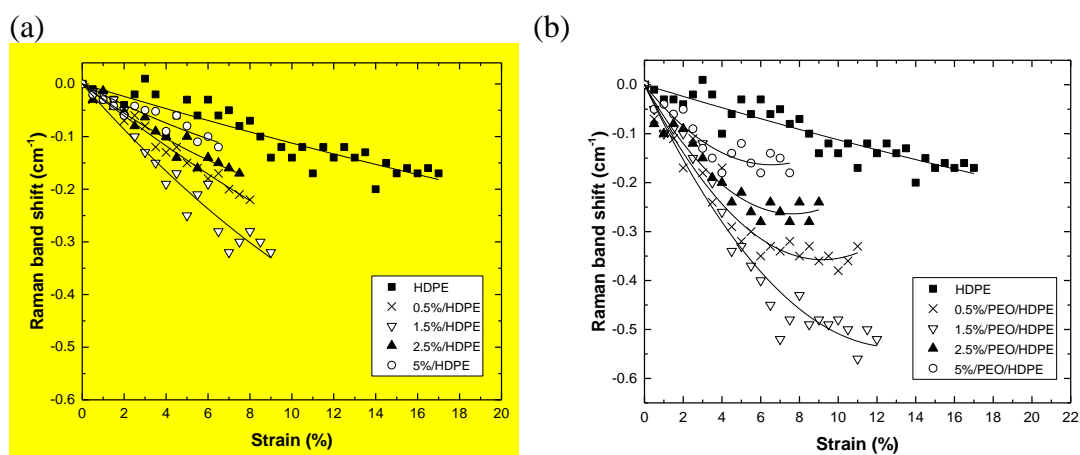


Figure 9 Typical shifts in the positions of Raman bands as a function of tensile strain initially located at $\sim 1132 \text{ cm}^{-1}$ for the pure polyethylene matrix and at $\sim 1095 \text{ cm}^{-1}$ for (a) unmodified-CNCs and (b) PEO-modified CNCs at a different filler weight fractions (0.5, 1.5, 2.5 and 5 wt%). Data are fitted with a 2nd order quadratic equation (solid line).

It is noted that in both Figures 8 and 9 the shift in the position of the band related to polyethylene ($\sim 1132\text{ cm}^{-1}$) is small, but non-zero. This result suggests that some load is borne by the matrix, but the majority of the stress is transferred from the lower stiffness matrix to the CNCs, which is typical for a fibre reinforced composite. Shifts in the peak position initially located at $\sim 1132\text{ cm}^{-1}$ were observed for samples containing CNCs (not shown), which suggests some load sharing between the two phases. Shifts in Raman peaks in polyethylene have been previously observed [26]. More highly oriented forms of polyethylene, such as fibres, might increase this shift and possibly the shift in the peaks emanating from cellulose, but this remains a topic for future research.

4. Conclusions

In this study, CNC-polyethylene composites were successfully fabricated by melt compounding and the structure-property relationships were investigated. A polyethylene oxide compatibiliser was successfully incorporated on the surface of the CNCs via a solution-mixing procedure followed by freeze drying. Improved thermal stability of the CNCs was observed showing the compatibilizing action of PEO. The crystallinity of the composites increases with the addition of CNCs up to a maximum at 1.5 wt.%. The composites comprising polyethylene with PEO-modified CNCs have a higher crystallinity than unmodified samples. This is thought to be due to the typical effect of a plasticised thermoplastic, where the plasticizer may promote crystallinity due to enhanced chain mobility. An optimum reinforcement weight fraction of 1.5 wt.% has been found for both unmodified and PEO-modified CNCs. A decrease in the crystallinity and mechanical properties is noted at higher concentrations (above 1.5 wt.%) for all composite samples. The improved mechanical properties of PEO-modified/HDPE

revealed that PEO can improve the interface between CNC and HDPE. The micromechanics of the composites have been investigated using Raman spectroscopy. The most efficient stress transfer was observed at 1.5 wt.% CNCs content. A decrease in the shift rate of a band located at $\sim 1095\text{ cm}^{-1}$, characteristic of cellulose, above 1.5 wt.% CNCs content has been found. This decrease is thought to be due to the aggregation of the CNCs at high weight fractions. The PEO-modified CNCs showed enhanced stress transfer compared to unmodified-CNCs. The strong interaction between CNCs and PEO, and the HDPE appears to play an important role in enhancing stress transfer between the matrix and CNCs.

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